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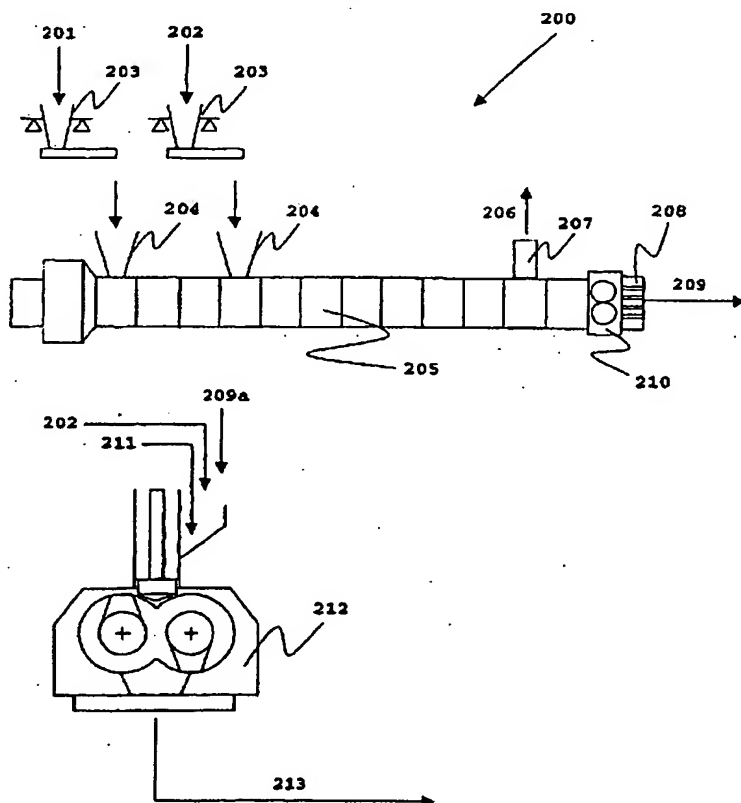
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(54) Title: METHOD FOR PREPARING A CROSSLINKABLE ELASTOMERIC COMPOSITION



(57) Abstract: Method for producing a crosslinkable elastomeric composition comprising: a) at least one thermoplastic polymer selected from amorphous polymers having a glass transition temperature ( $T_g$ ) higher than 80 °C or crystalline polymers having a melting temperature ( $T_m$ ) higher than 190 °C; b) at least one diene elastomeric polymer; said method comprising the following steps: pre-mixing said at least thermoplastic polymer (a) with a portion of said diene elastomeric polymer (b) to obtain a masterbatch; said pre-mixing step being carried out at a temperature not lower than  $T_g$  or not lower than ( $T_m - 20$  °C); mixing the masterbatch obtained in said pre-mixing step (1) to the remaining portion of said diene elastomeric polymer (b).

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METHOD FOR PREPARING A CROSSLINKABLE ELASTOMERIC  
COMPOSITION

The present invention relates to a method for  
5 preparing a crosslinkable elastomeric composition.

More particularly, the present invention relates  
to a method for preparing a crosslinkable  
elastomeric composition, said elastomeric  
composition comprising at least one diene  
10 elastomeric polymer and at least one thermoplastic  
polymer.

The present invention also relates to an  
elastomeric composition comprising at least one  
diene elastomeric polymer and at least one  
15 thermoplastic polymer.

In the rubber industry, in particular that of  
tyres for vehicles wheels, the use of thermoplastic  
polymers in elastomeric compositions in order to  
improve their mechanical properties (both static and  
20 dynamic), has been described. The improvement of  
said mechanical properties, in particular of said  
dynamic mechanical properties, depending on the  
thermoplastic polymer used, allows to obtain tyres  
having either a low rolling resistance at the normal  
25 working temperatures (40°C - 70°C) of the tyres or a  
good roadholding at higher temperatures following  
high thermomechanical stresses such as, for example,  
those derived from driving the vehicle under "hard  
handling" conditions .

For example, European patent application EP  
30 117,834 describes a tyre with a tread band  
consisting of a sulphur-crosslinked elastomeric  
composition which includes a dispersion comprising  
from about 2 phr to about 15 phr, preferably from  
35 about 3 phr to about 10 phr, of a polystyrene resin

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in the form of particles with a softening point of between about 90°C and about 120°C, preferably between about 90°C and about 110°C. The presence of said polystyrene resin in the tread band of the tyre is said to increase the holding on wet surfaces while keeping the rolling resistance unchanged under the normal conditions of use, and to ensure holding under conditions of particularly high friction. In this respect, the following explanation is given.

When the temperature of the tread band reaches 120°C-150°C or higher values, due to particularly high friction conditions, and thus temperature values above the softening point of the polystyrene resin, the outer part of the tread band softens and this is believed to allow an increase in traction and better roadholding of the tyre. On the other hand, during normal use of the tyre, up to temperatures of about 70°C, and thus temperature values below the softening point of the polystyrene resin, said resin remains passive and the tyre maintains low rolling resistance values.

European patent application EP 1,029,874 describes a polymer resin derived from the polymerization of limonene, dicyclopentadiene and t-butylstyrene, for use in elastomeric compositions for manufacturing tyre tread bands. The presence of said polymer resin in the tyre tread band is said to make it possible to obtain an increase in holding on dry surfaces without having an adverse effect on the durability of the tyre.

European patent application EP 1,063,246 describes a polymer resin derived from the polymerization of limonene, dimethyldicyclopentadiene, indene and vinyltoluene, for use in elastomeric compositions for manufacturing tyre

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tread bands. The presence of said polymer resin in the tyre tread band is said to make it possible to obtain an increase in the holding on dry surfaces without having an adverse effect on the durability of the tyre.

European patent application EP 1,050,547 describes a polymer resin derived from the polymerization of limonene and dimethyldicyclopentadiene for use in elastomeric compositions for manufacturing tyre tread bands. The presence of said polymer resin in the tyre tread band is said to make it possible to obtain an increase in the holding on dry surfaces without having an adverse effect on the durability of the tyre.

European patent application EP 754,571 describes a crosslinkable elastomeric composition comprising a polymer base containing a crosslinkable unsaturated chain and at least one organic compound which is solid at ambient temperature, said compound being substantially insoluble in the polymer base and having a first-order or second-order transition temperature of between 80°C and 160°C and an average molecular weight of between 10,000 and 1,000,000. Said organic compound is selected from polyphenylenether (such as, for example, Vestoran® 1100 from Hüls), polyethylene, polypropylene, polymethyl methacrylate, polyvinyl alcohol, ethylene/vinyl alcohol copolymers, acrylonitrile/butadiene/styrene (ABS) terpolymers, ethylene/methacrylic acid copolymers, styrene/isoprene (SIS), styrene/butadiene (SBS), styrene/ethylene-butylene/styrene (S-E/B-S) and styrene/ethylene-propylene (S/E-P) block copolymers, or mixtures thereof. The abovementioned elastomeric composition may be used to prepare tread bands and

is said to make it possible to obtain tyres with both low rolling resistance at the normal temperatures of use (40°C-70°C) and high roadholding when the tyre exceeds said temperatures due to high thermomechanical stresses.

US patent 4,487,892 describes a rubber composition for use in tyres which comprises 1%-30% by weight of a non-crystallizable resinous polymer having a glass transition temperature ( $T_g$ ) of not less than 110°C and 70%-99% by weight of at least one rubber selected from styrene/butadiene copolymer rubber containing not more than 60% by weight of bound styrene, natural rubber, polybutadiene rubber having 1,4-configuration of not less than 80%, polybutadiene rubber having 1,2-configuration of not less than 50%, butyl rubber, halogenated butyl rubber and polyisoprene rubber having cis-1,4-configuration of not less than 90%. Said non-crystallizable resinous polymer is selected from:  $\alpha$ -methylstyrene homopolymer,  $\alpha$ -methylstyrene/styrene copolymer, nuclear-substituted styrene homopolymer, nuclear-substituted  $\alpha$ -methylstyrene homopolymer, styrene-nuclear-substituted styrene copolymer, styrene-nuclear-substituted  $\alpha$ -methylstyrene copolymer, and copolymers thereof containing a diene monomer. The abovementioned rubber composition may be used to prepare tread bands and is said to make it possible to obtain tyres having high driving performances, i.e. considerably improved controllability and stability during high-speed running.

US patent 4,427,831 describes a rubber material comprising a mixture of an ordinary rubber and a powder of norbornene polymer which hardens at service temperature on ice and softens at higher

temperatures and which does not lose its shape as a powder when heated during curing or shaping. Said ordinary rubber is selected from: butadiene rubber, styrene-butadiene rubber, isoprene rubber, or a  
5 natural rubber. The abovementioned rubber material may be formed into rubber articles such as tyres and shoes soles which have an excellent grip on ice.

US patent 4,166,083 describes a rubber composition comprising (a) 70% to 90% by weight of  
10 at least one diene rubber, and (b) 30% to 5% by weight of a polymer or copolymer obtained by polymerizing at least one norbornene compound. The abovementioned rubber composition, which may be used in tyres manufacturing, is said to have high green  
15 strength and improved tensile modulus, abrasion resistance and wet skid resistance.

However, the use of thermoplastic polymers in elastomeric compositions shows some drawbacks.

According to the Applicant's experience, the  
20 elastomeric compositions comprising thermoplastic polymers obtained according to the known techniques, does not satisfy the various requirements that render their use actually advantageous in the manufacture of cross-linked products, in particular  
25 in the manufacture of tyres. In particular, Applicant noticed that said thermoplastic polymers are not homogeneously dispersed in the elastomeric base: consequently, the resulting elastomeric compositions, because of formation of coarse  
30 particles having large dimensions (usually with an average diameter of about 100  $\mu\text{m}$  or more), once crosslinked, show unsatisfactory mechanical properties, both static (in particular stress at break) and dynamic (in particular modulus and  
35 tandelta).

The Applicant has now found that it is possible to obtain a crosslinkable elastomeric composition comprising at least one thermoplastic polymer and at least one diene elastomeric polymer, capable of  
5 being advantageously used in the manufacture of crosslinked manufactured products, in particular in the manufacture of tyres, by using a thermoplastic polymer having a high glass transition temperature (e.g. higher than 80°C) or a high melting  
10 temperature (e.g. higher than 190°C) in the form of a masterbatch, said masterbatch being obtained by previously mixing said thermoplastic polymer with a portion of said diene elastomeric polymer. Subsequently, said masterbatch is added to the  
15 remaining portion of said diene elastomeric polymer obtaining a crosslinkable elastomeric composition which shows improved, both static and dynamic, mechanical properties.

According to a first aspect, the present  
20 invention thus relates to a method for producing a crosslinkable elastomeric composition comprising:

(a) at least one thermoplastic polymer selected from amorphous polymers having a glass transition temperature ( $T_g$ ) higher than 80°C or crystalline  
25 polymers having a melting temperature ( $T_m$ ) higher than 190°C;

(b) at least one diene elastomeric polymer;

said method comprising the following steps:

- pre-mixing said thermoplastic polymer (a) with a  
30 portion of said diene elastomeric polymer (b) to obtain a masterbatch, said pre-mixing step being carried out at a temperature not lower than  $T_g$  or not lower than ( $T_m - 20^\circ\text{C}$ );
- mixing the masterbatch obtained in said pre-  
35 mixing step to the remaining portion of said



diene elastomeric polymer (b).

Said glass transition temperature ( $T_g$ ) and said melting temperature ( $T_m$ ) may be determined by known techniques such as, for example, by DSC  
5 (Differential Scanning Calorimetry). Alternatively, said glass transition temperature ( $T_g$ ) may be determined according to ISO standard 306 (Vicat point).

The abovementioned method may be carried out in  
10 continuously or discontinuously.

According to one preferred embodiment, in said pre-mixing step the portion of the diene elastomeric polymer (b) used is from 20% by weight to 90% by weight, preferably from 30% by weight to 50% by  
15 weight, with respect to the weight of the diene elastomeric polymer (b) present in the final crosslinkable elastomeric composition.

According to one preferred embodiment, said thermoplastic polymer (a) is present in the  
20 crosslinkable elastomeric composition in an amount of from 0.1 phr to 100 phr, preferably from 3 phr to 60 phr, even more preferably from 5 phr to 40 phr.

For the purposes of the present description and of the claims which follows, the term "phr" means  
25 the parts by weight of a given component of the elastomeric composition per 100 parts by weight of the diene elastomeric polymer.

According to one preferred embodiment, said pre-mixing step comprises:

- 30 - feeding at least one thermoplastic polymer (a) into at least one extruder comprising a housing, at least one screw rotatably mounted in said housing including at least one feed opening and a discharge opening;
- 35 - mixing said at least one thermoplastic polymer

- (a) at a temperature not lower than  $T_g$  or not lower than  $(T_m - 20^\circ\text{C})$ ;
- feeding at least one diene elastomeric polymer (b);
  - 5 - mixing said at least one diene elastomeric polymer (b);
  - dispersing said at least one thermoplastic polymer (a) into said at least one diene elastomeric polymer (b) to obtain a masterbatch;
  - 10 - extruding the obtained masterbatch through the discharge opening of said extruder.

Preferably, said extruder is a co-rotating twin-screw extruder.

- Said masterbatch may be obtained in the form of
- 15 a continuous ribbon or, alternatively, in the form of a subdivided product.

- According to a preferred embodiment, said at least one thermoplastic polymer (a) is dispersed in said masterbatch in the form of particles having an
- 20 average diameter not higher than  $20\text{ }\mu\text{m}$ , preferably of between  $8\text{ }\mu\text{m}$  and  $18\text{ }\mu\text{m}$ .

According to a further aspect, the present invention relates to an elastomeric composition comprising:

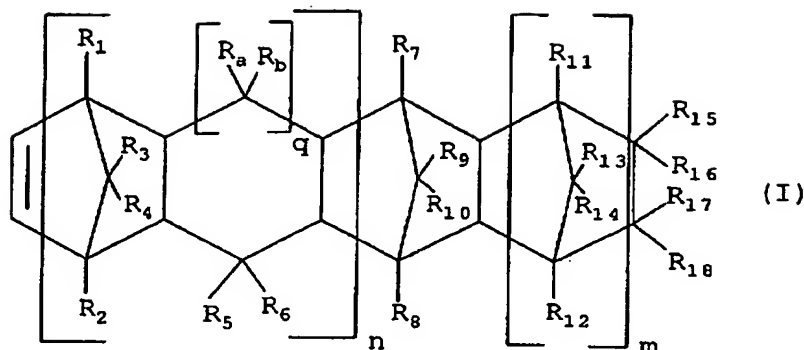
- 25 - from 1% to 65%, preferably from 10% to 40%, of at least one thermoplastic polymer (a), said thermoplastic polymer (a) being selected from amorphous polymers having a glass transition temperature ( $T_g$ ) higher than  $80^\circ\text{C}$  or crystalline
- 30 polymers having a melting temperature ( $T_m$ ) higher than  $190^\circ\text{C}$ ;
- from 35% to 99%, preferably from 60% to 90%, of at least one diene elastomeric polymer (b);
- wherein said at least one thermoplastic polymer (a)
- 35 is dispersed in said elastomeric composition in the

form of particles having an average diameter not higher than 20  $\mu\text{m}$ , preferably of between 8  $\mu\text{m}$  and 18  $\mu\text{m}$ .

According to one preferred embodiment, the thermoplastic polymer (a) may be selected, for example, from: cycloolefin polymers, poly(phenylene ethers), styrene-based polymers, polyesters, polyamides, polyimides, polycarbonates, polysulfones, polyvinylchlorides, polymethyl(meth)acrylates, polyacrylonitriles, polyvinylpyrrolidones, aromatic polyketones, poly(alkylene oxides), aromatic polysulphides, perfluorurated polyalkylenes, or mixtures thereof. Cycloolefin polymers, poly(phenylene-ethers), styrene-based polymers and polyesters, are particularly preferred.

Cycloolefin polymers which may be used in the present invention may be selected, for example, from:

- (b-1) a cycloolefin random copolymer obtained by copolymerizing (i) at least one aliphatic  $\alpha$ -olefin and (ii) at least one cycloolefin represented by the following formula (I) and, optionally, (iii) a polyene;
- (b-2) a ring-opening polymer of at least one cycloolefin represented by the following formula (I); and
- (b-3) a hydrogenation product of a ring-opening polymer of at least one cycloolefin represented by the following formula (I):



wherein:

- n is 0 or a positive integer, preferably is 0 or 1;
- 5 - m is 0 or a positive integer;
- q is 0 or 1;
- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>a</sub> and R<sub>b</sub>, which may be equal or different from each other, represent a
- 10 hydrogen atom, a halogen atom, or an aliphatic, an alicyclic or an aromatic hydrocarbon group;
- R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, may be linked each other to form a monocyclic or polycyclic group which may have double bonds; and
- 15 - R<sub>15</sub> and R<sub>16</sub>, or R<sub>17</sub> and R<sub>18</sub>, may together form an alkylidene group.

The term "aliphatic  $\alpha$ -olefin" generally means an olefin of formula  $\text{CH}_2=\text{CH}-\text{R}$ , in which R represents a hydrogen atom, a linear or branched alkyl group

20 containing from 1 to 12 carbon atoms. Preferably, the aliphatic  $\alpha$ -olefin is selected from: ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene,

25

or mixture thereof. Of these, preferred is ethylene or propylene, particularly preferred is ethylene.

Examples of the halogen atom include fluorine atom, chlorine atom, bromine atom and iodine atom.

5 Examples of the hydrocarbon group generally include alkyl group having from 1 to 20 carbon atoms, cycloalkyl group having from 3 to 15 carbon atoms, and aromatic hydrocarbon group having from 6 to 14 carbon atoms.

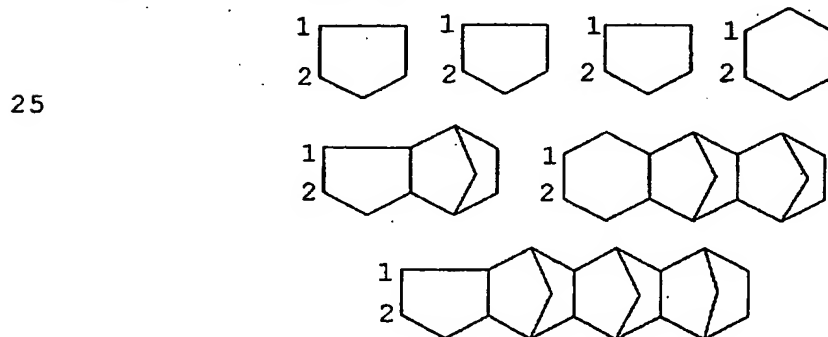
10 Specific examples of the alkyl group include methyl, propyl, isopropyl, amyl, octyl, decyl, dodecyl, octadecyl, these alkyl groups may be substituted with halogen atoms.

15 A specific example of the cycloalkyl group is cyclohexyl.

Specific examples of the aromatic hydrocarbon group include phenyl, naphthyl.

Moreover, in the above formula (I),  $R_{15}$  and  $R_{16}$ ,  $R_{17}$  and  $R_{18}$ ,  $R_{15}$  and  $R_{17}$ ,  $R_{16}$  and  $R_{18}$ ,  $R_{15}$  and  $R_{18}$ , or  $R_{16}$  and  $R_{17}$ , may be linked together to form a monocyclic or polycyclic group, optionally containing a double bonds.

Examples of the monocyclic or polycyclic group are the following:



wherein carbon atoms attached with numerals 1 and 2 are those to which substituent  $R_{15}$  or  $R_{16}$  and  $R_{17}$  or

R<sub>18</sub> are linked respectively.

In the above formula (I), R<sub>15</sub> and R<sub>16</sub> or R<sub>17</sub> and R<sub>18</sub> may together form an alkylidene group. This alkylidene group generally has from 2 to 20 carbon atoms and, examples of such alkylidene group include ethylidene, propylidene, isopropylidene.

In the above formula (I), when q is 1, the corresponding ring is a 6-membered ring and, when q is 0, the corresponding ring is a 5-membered ring.

Preferably, the cycloolefin polymer (b) which may be used in the present invention may be selected from copolymers of a cyclic olefin having a norbornene-based structure (preferably norbornene, tetracyclododecene or cyclic olefins - having a structure derived from them), and an aliphatic  $\alpha$ -olefin (preferably ethylene or propylene). Among them, norbornene-ethylene copolymer, norbornene-propylene copolymer, tetracyclododecene-ethylene copolymer, tetracyclododecene-propylene copolymer, are particularly preferred. More particularly, norbornene-ethylene copolymer is preferred.

With reference to a cycloolefin random copolymer (b-1), the term "polyene" generally means a conjugated or non-conjugated diene, triene or tetraene. When a diene comonomer is present, this comonomer generally contains from 4 to 20 carbon atoms and is preferably selected from: linear conjugated or non-conjugated diolefins such as, for example, 1,3-butadiene, 1,4-hexadiene, 1,6-octadiene; monocyclic or polycyclic dienes such as, for example, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, vinylnorbornene, or mixtures thereof. When a triene or tetraene comonomer is present, this comonomer generally contains from 9 to 30 carbon atoms and is

preferably selected from trienes or tetraenes containing a vinyl group in the molecule or a 5-norbornen-2-yl group in the molecule. Specific examples of triene or tetraene comonomers which may  
5 be used in the present invention are: 6,10-dimethyl-1,5,9-undecatriene, 5,9-dimethyl-1,4,8-decatriene, 6,9-dimethyl-1,5,8-decatriene, 6,8,9-trimethyl-1,6,8-decatriene, 6,10,14-trimethyl-1,5,9,13-pentadecatetraene, or mixture thereof. Preferably,  
10 the polyene is a diene.

Usually, the cycloolefin polymer (b) as described above, has an intrinsic viscosity  $[\eta]$  as measured in decalin at 135°C, of from 0.01 dl/g to 10 dl/g, preferably from 0.05 dl/g to 5 dl/g, more-preferably  
15 0.3 dl/g to 2 dl/g.

The cycloolefin random copolymer (b-1) generally has the following composition: 40 mol%-85 mol%, preferably 42 mol%-80 mol%, of an aliphatic  $\alpha$ -olefin; 15 mol%-60 mol%, preferably 20 mol%-58 mol%  
20 of a cycloolefin having formula (I); 0 mol%-10 mol%, preferably 0 mol%-2 mol%, of a polyene.

The random cycloolefin copolymers (b-1), (b-2) e (b-3) may be synthesized by using any polymerization technique known in the art. Examples of said  
25 techniques are disclosed, for example, in the following US patents: US 5,494,969, US 5,741,869 and US 5,569,711.

Examples of cycloolefin random copolymers (b-1) which may be used in the present invention and which  
30 are currently commercially available are the products Topas® from Ticona.

Poly(phenylene ethers) (PPE) which may be used in the present invention may be selected, for example, from thermoplastic engineering resins  
35 obtained by the oxidative coupling polymerization of

alkyl substituted phenols. Examples of said thermoplastic engineering resins include poly(2,6-dialkyl-1,4-phenylene ethers) such as, for example, poly(2,6-dimethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2,6-dipropyl-1,4-phenylene ether), poly(2-ethyl-6-propyl-1,4-phenylene ethers), or mixtures thereof.

Examples of poly(phenylene) ethers which may be used in the present invention and which are currently commercially available are the products Vestoran® from Degussa Hüls.

Styrene-based polymers which may be used in the present invention may have atactic, syndiotactic or isotactic configuration. Examples of said styrene-based polymers are: polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(halogenated alkylstyrene), poly(alkoxystyrene), poly(vinyl benzoate), hydrogenated polymer thereof, or mixtures thereof. The poly(alkylstyrene) includes poly(methylstyrene), poly(ethylstyrene), poly(isopropylstyrene), poly(t-butylstyrene), poly(phenylstyrene), poly(vinylnaphthalene), polyvinyl(styrene), or mixtures thereof. Poly(halogenated styrene) includes poly(chlorostyrene), poly(bromostyrene), poly(fluorostyrene), or mixtures thereof. The poly(halogenated alkylstyrene) includes poly(chloromethylstyrene). The poly(alkoxystyrene) includes poly(methoxystyrene), poly(ethoxystyrene), or mixtures thereof.

Examples of styrene-based polymers which may be used in the present invention and which are currently commercially available are the products Edistir® from Polimeri Europa and Questra® from Dow Plastic.

Polyesters which may be used in the present



invention may be selected, for example, from the polymer reaction products of at least one aliphathic or aromatic polycarboxylic acid ester of anhydride and at least a diol. Examples of said polyesters are:

5 poly(trans-1,4-cyclohexylene-(C<sub>2</sub>-C<sub>6</sub>)-alkane dicarboxylates such as, for example, poly(trans-1,4-cyclohexylene succinate, poly(trans-1,4-cyclohexylene adipate); poly(cis- or trans-1,4-cyclohexanedimethylene)alkanedicarboxylates such as,

10 for example, poly(cis-1,4-cyclohexanedimethylene)oxalate, poly(cis-1,4-cyclohexanedimethylene)succinate; poly-(C<sub>2</sub>-C<sub>4</sub>)-alkylene terephthalates such as, for example, polyethylene terephthalate, polybutylene

15 terephthalate, polytetramethylene terephthalate; poly-(C<sub>2</sub>-C<sub>4</sub>)-alkylene isophthalates such as, for example, polyethylene isophthalate, polytetramethylene isophthalate, or mixtures thereof.

20 Examples of polyesters which may be used in the present invention and which are currently commercially available are the products Vestodur® from Degussa Hüls.

Said thermoplastic polymer (a), either amorphous

25 or crystalline, may optionally contain functional groups selected from: hydroxy groups, carboxylic groups, anhydride groups, ester groups, silane groups, epoxide groups. The amount of functional groups present in the thermoplastic polymer is

30 generally between 0.05 and 50 parts by weight, preferably between 0.1 and 10 parts by weight, relative to 100 parts by weight of thermoplastic polymer (a).

The functional groups may be introduced during

35 the production of the thermoplastic polymer (a), by

copolymerization with corresponding functionalized monomers containing at least one ethylenic unsaturation, or by subsequent modification of the thermoplastic polymer (a) by grafting said  
5 functionalized monomers in the presence of a free-radical initiator (in particular an organic peroxide).

Functionalized monomers which may be used, for example, are: silanes containing at least one  
10 ethylenic unsaturation; epoxides containing at least one ethylenic unsaturation; monocarboxylic or, preferably, dicarboxylic acids containing at least one ethylenic unsaturation, or derivatives thereof, in particular anhydrides or esters. -

15 Examples of silanes containing at least one ethylenic unsaturation are:  $\gamma$ -methacryloxypropyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, allylmethyldimethoxysilane, allylmethyldiethoxysilane, vinyltris(2-methoxyethoxy)silane,  
20 vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyltriethoxysilane, or mixtures thereof.

Examples of epoxides containing at least one ethylenic unsaturation are: glycidyl acrylate,  
25 glycidyl methacrylate, monoglycidyl ester of itaconic acid, glycidyl ester of maleic acid, vinyl glycidyl ether, allyl glycidyl ether, or mixtures thereof.

Examples of monocarboxylic or dicarboxylic acids containing at least one ethylenic unsaturation, or derivatives thereof, are: maleic acid, maleic  
30 anhydride, fumaric acid, citraconic acid, itaconic acid, acrylic acid, methacrylic acid, or mixtures thereof, and anhydrides or esters derived therefrom, or mixtures thereof.  
35

According to one preferred embodiment, the diene elastomeric polymer (b) which may be used in the present invention may be selected from those commonly used in sulphur-crosslinkable elastomeric compositions, that are particularly suitable for producing tyres, that is to say from elastomeric polymers or copolymers with an unsaturated chain having a glass transition temperature ( $T_g$ ) generally below 20°C, preferably in the range of from 0°C to -90°C. These polymers or copolymers may be of natural origin or may be obtained by solution polymerization, emulsion polymerization or gas-phase polymerization of one or more conjugated diolefins, optionally blended with at least one comonomer selected from monovinylarenes and/or polar comonomers in an amount of not more than 60% by weight.

The conjugated diolefins generally contain from 4 to 12, preferably from 4 to 8 carbon atoms, and may be selected, for example, from the group comprising: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene, or mixtures thereof. 1,3-butadiene and isoprene are particularly preferred.

Monovinylarenes which may optionally be used as comonomers generally contain from 8 to 20, preferably from 8 to 12 carbon atoms, and may be selected, for example, from: styrene; 1-vinylnaphthalene; 2-vinylnaphthalene; various alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl derivatives of styrene such as, for example,  $\alpha$ -methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-

phenylbutyl)styrene, or mixtures thereof. Styrene is particularly preferred.

- Polar comonomers which may optionally be used may be selected, for example, from: vinylpyridine, vinylquinoline, acrylic acid and alkylacrylic acid esters, nitriles, or mixtures thereof, such as, for example, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile, or mixtures thereof.
- Preferably, the diene elastomeric polymer (b) which may be used in the present invention may be selected, for example, from: cis-1,4-polyisoprene (natural or synthetic, preferably natural rubber), 3,4-polyisoprene, polybutadiene (in particular polybutadiene with a high 1,4-cis content), optionally halogenated isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, styrene/1,3-butadiene copolymers, styrene/isoprene/1,3-butadiene copolymers, styrene/1,3-butadiene/acrylonitrile copolymers, or mixtures thereof.

- The elastomeric composition according to the present invention may optionally comprise at least one elastomeric polymer of one or more monoolefins with an olefinic comonomer or derivatives thereof (c). The monoolefins may be selected from: ethylene and  $\alpha$ -olefins generally containing from 3 to 12 carbon atoms, such as, for example, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, or mixtures thereof. The following are preferred: copolymers between ethylene and an  $\alpha$ -olefin, optionally with a diene; isobutene homopolymers or copolymers thereof with small amounts of a diene, which are optionally at least partially halogenated. The diene optionally present generally contains from 4 to 20 carbon atoms

and is preferably selected from: 1,3-butadiene, isoprene, 1,4-hexadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, vinylnorbornene, or mixtures thereof. Among these, the following are particularly preferred: ethylene/propylene copolymers (EPR) or ethylene/propylene/diene copolymers (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers, in particular chlorobutyl or bromobutyl rubbers; or mixtures thereof.

A diene elastomeric polymer (b) or an elastomeric polymer (c) functionalized by reaction with suitable terminating agents or coupling agents may also be used. In particular, the diene elastomeric polymers obtained by anionic polymerization in the presence of an organometallic initiator (in particular an organolithium initiator) may be functionalized by reacting the residual organometallic groups derived from the initiator with suitable terminating agents or coupling agents such as, for example, imines, carbodiimides, alkyltin halides, substituted benzophenones, alkoxysilanes or aryloxysilanes (see, for example, European patent EP 451 604, or patents US 4 742 124 and US 4 550 142).

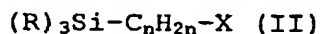
At least one reinforcing filler may advantageously be added to the elastomeric composition according to the present invention, in an amount generally of from 0.1 phr to 120 phr, preferably from 20 phr to 90 phr. The reinforcing filler may be selected from those commonly used for crosslinked manufactured products, in particular for tyres, such as, for example, carbon black, silica, alumina, aluminosilicates, calcium carbonate, kaolin, or mixtures thereof.

The types of carbon black which may be used according to the present invention may be selected from those conventionally used in the production of tyres, generally having a surface area of not less  
5 than 20 m<sup>2</sup>/g (determined by CTAB absorption as described in ISO standard 6810).

The silica which may be used according to the present invention may generally be a pyrogenic silica or, preferably, a precipitated silica, with a  
10 BET surface area (measured according to ISO standard 5794/1) of from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, preferably from 70 m<sup>2</sup>/g to 200 m<sup>2</sup>/g.

When a reinforcing filler comprising silica is present, the elastomeric composition may  
15 advantageously incorporate a coupling agent capable of interacting with the silica and of linking it to the diene elastomeric polymer during the vulcanization.

Coupling agents that are preferably used are  
20 those based on silane which may be identified, for example, by the following structural formula (II):



in which the groups R, which may be identical or different, are selected from: alkyl, alkoxy or  
25 aryloxy groups or from halogen atoms, on condition that at least one of the groups R is an alkoxy or aryloxy group; n is an integer between 1 and 6 inclusive; X is a group selected from: nitroso, mercapto, amino, epoxide, vinyl, imide, chloro, -  
30 (S)<sub>m</sub>C<sub>n</sub>H<sub>2n</sub>-Si-(R)<sub>3</sub> in which m and n are integers between 1 and 6 inclusive and the groups R are defined as above.

Among the coupling agents that are particularly preferred are bis(3-triethoxysilylpropyl)  
35 tetrasulphide and bis(3-triethoxysilylpropyl)

disulphide. Said coupling agents may be used as such or as a suitable mixture with an inert filler (for example carbon black) so as to facilitate their incorporation into the elastomeric composition.

5       The elastomeric composition according to the present invention may be vulcanized according to known techniques, in particular with sulphur-based vulcanizing systems commonly used for diene elastomeric polymers.

10       The vulcanizing agent most advantageously used is sulphur, or molecules containing sulphur (sulphur donors), with accelerators and activators known to those skilled in the art.

15       Activators that are particularly effective are zinc compounds, and in particular ZnO, ZnCO<sub>3</sub>, zinc salts of saturated or unsaturated fatty acids containing from 8 to 18 carbon atoms, such as, for example, zinc stearate, which are preferably formed in situ in the elastomeric composition from ZnO and  
20       fatty acid, and also BiO, PbO, Pb<sub>3</sub>O<sub>4</sub>, PbO<sub>2</sub>, or mixtures thereof.

25       Accelerators that are commonly used may be selected from: dithiocarbamates, guanidine, thiourea, thiazoles, sulphenamides, thiurams, amines, xanthates, or mixtures thereof.

30       The elastomeric composition according to the present invention may comprise other commonly used additives selected on the basis of the specific application for which the composition is intended. For example, the following may be added to said composition: antioxidants, anti-ageing agents, plasticizers, adhesives, anti-ozone agents, modifying resins, fibres (for example Kevlar® pulp), or mixtures thereof.

35       In particular, for the purpose of further

improving the processability, a plasticizer generally selected from mineral oils, vegetable oils, synthetic oils, or mixtures thereof, such as, for example, aromatic oil, naphthenic oil, phthalates, soybean oil, or mixtures thereof, may be added to the elastomeric composition according to the present invention. The amount of plasticizer generally ranges from 2 phr to 100 phr, preferably from 5 phr to 50 phr.

10 The mixing of the masterbatch obtained in the pre-mixing step to the remaining portion of the diene elastomeric polymer (b), may be carried out discontinuously or continuously.

When the process is carried out discontinuously (see Fig. 1), the mixing of the remaining portion of the diene elastomeric polymer (b) with the masterbatch of the thermoplastic polymer (a) and with the other components optionally present, is carried out, for example, using an open internal mixer such as an open mill, or an internal mixer of the type with tangential rotors (Banbury) or with interlocking rotors (Intermix).

When said process is carried out continuously (see Fig. 2 and Fig. 3), the mixing of the diene elastomeric polymer (b) with the masterbatch of the thermoplastic polymer (a) and with the other components optionally present, is carried out, for example, using a continuous mixer such as a Ko-Kneader mixer (Buss) or using a co-rotating or a counter-rotating twin-screw extruder or a single-screw extruder.

During the mixing, the temperature is kept below a predetermined value so as to avoid premature crosslinking of the composition. To this end, the temperature is generally kept below 170°C,



preferably below 150°C, even more preferably below 120°C. As regards the mixing time, this may vary within a wide range, depending mainly on the specific composition of the mixture, on the presence  
5 of reinforcing fillers and on the type of mixer used. In general, a mixing time of more than 10 seconds, preferably between 1 minute and 35 minutes is sufficient to obtain a homogeneous composition.

Preferably, the mixing is carried out in two  
10 steps. Preferably, an intermediate elastomeric composition is obtained (1<sup>st</sup> step) by mixing the diene elastomeric polymer (b), the masterbatch of the thermoplastic polymer (a), the reinforcing fillers and the minor ingredients which are non  
15 temperature sensitive, namely, those ingredients which do not degrade and/or cause scorching at the operating conditions and/or do not interfere with the compounding process. Generally, said non temperature sensitive minor ingredients are all the  
20 minor ingredients except crosslinking agents, crosslinking accelerators, crosslinking retardants and crosslinking activators. For instance, it is to be avoided to use in the 1<sup>st</sup> step those minor ingredients which can interfere with reactions that  
25 may occur during said 1<sup>st</sup> step. For example, in the case of silica filled rubber mixtures, zinc derivatives (e.g. ZnO) and amine compounds should not be added during said 1<sup>st</sup> step since they can interfere with the silanization reaction between the  
30 coupling agent and silica.

The present invention will now be illustrated in further detail by means of a number of illustrative embodiments, with reference to the attached figures wherein:

35 - Fig 1 is a schematic diagram of a batchwise

production plant for producing an elastomeric composition according to the present invention;

- Fig. 2 is a schematic diagram of a continuous production plant for producing an elastomeric composition according to the present invention;
- 5 - Fig. 3 is a schematic diagram of a further embodiment of a continuous production plant for producing an elastomeric composition according to the present invention;
- 10 - Fig. 4, is a view in cross section of a portion of a tyre made according to the invention.

With reference to Fig. 1, the batchwise production plant (200) includes an extruder (205) suitable for producing a masterbatch according to  
15 the present invention. As schematically shown in Fig. 1, by means of two feed hoppers (204) the extruder (205) is fed with the ingredients necessary for producing said desired masterbatch which typically comprises the following ingredients: at  
20 least one thermoplastic polymers (a) and at least one diene elastomeric polymers (b), as defined above.

Preferably, the extruder (205) is a co-rotating twin screw extruder.

25 Generally, said ingredients are fed to different zone of the extruder. For example, Fig. 1 shows two main flows (201) and (202) in correspondence of two different zones of the extruder (205).

The same ingredient may be fed to the extruder  
30 in distinct portions, for example the same ingredient may be fed to two or more distinct zones of the extruder. For example, the diene elastomeric polymer (b) is fed to two distinct zones of the extruder. Therefore, each feed hopper may comprise  
35 more than one ingredient: for example, a portion of

a diene elastomeric polymer (b) may be fed to the extruder (205) through the first feed hopper (204) together with the thermoplastic polymer (a), the remaining portion of said diene elastomeric polymer (b) being fed through the second feed hopper (204).

Each flow (201) and (202) are fed to the feed hoppers (204) by means of a metering device (203). Preferably, said metering device (203) is a loss-in-weight gravimetric feeder.

For simplicity, Fig. 1 shows only one metering device (203) for each flow (201) and (202). However in the case each flow comprises more than one ingredient, preferably each ingredient is provided with a dedicated metering device. Alternatively, a plurality of different ingredients may be metered by means of the same metering device.

Before being fed to the metering device (203), the diene elastomeric polymer (b) (202), which is usually provided by manufacturers in bales, is comminuted in irregular particles (crumbs) of small size (about 3 mm - 15 mm as average dimensions), e.g. by of a rubber grinding (not represented in Fig. 1). The rubber crumbs may be then supplemented with an antisticking agent (e.g. chalk, silica, or other powders) to avoid reagglomeration.

The extruder (205) may optionally be provided with gravimetrically controlled feeding pumps (not represented in Fig. 1) which are useful to introduce into the extruder (205) plasticizing oils and possibly other liquid ingredients.

Fig. 1 shows also a degassing unit schematically indicated by reference sign (207) from which a flow (206) exits.

The masterbatch (209) is discharged from the extruder (205), e.g. in the form of a subdivided

product (209a) by pumping it through an extruder die (208) by means of a gear pump (210), said extruder die (208) being provided with a perforated die plate equipped with knives (not represent in Fig. 1).  
5 Alternatively, the masterbatch may be obtained in the form of a continuous ribbon which may be then granulated by means of a grinding device (not represented in Fig. 1). The obtained product in subdivided form is then cooled, e.g. by conveying it  
10 to a cooling device (not represented in Fig. 1).

The obtained product in subdivided form (209a), the remaining portion of the diene elastomeric polymer (202) and the other additives optionally present (211), are then fed to an internal mixer  
15 (212) (e.g. a Banbury mixer) obtaining an elastomeric composition according to the present invention.

Fig. 2 represents a continuous production plant (213) wherein the step of obtaining the elastomeric  
20 composition is carried out in a second extruder (305). To this end, the product in subdivided form (209a) obtained as disclosed above, the remaining portion of a diene elastomeric polymer (b) (202) and the other additive optionally present (211), are fed  
25 to the second extruder through feed hoppers (304) by means of metering devices (303).

Fig. 2 shows also a degassing unit schematically indicated by reference sign (307) from which a flow (306) exits.

30 The elastomeric composition (213) is discharged from the extruder (305) by pumping it through an extruder die (308) by means of a gear pump (310) in the form of a continuous ribbon which may be transformed into a subdivided product operating as  
35 disclosed above (not represented in Fig. 2).

Fig. 3 is a further embodiment of a continuous production plant (214) wherein the elastomeric composition according to the present invention is carried out by means of a single extruder (205). To this end the thermoplastic polymer (a) (201) and a portion of the diene elastomeric polymer (b) (202) is fed to the extruder (205) through fed hoppers (204) by means of metering devices (203).

After mixing, the remaining portion of the diene elastomeric polymer (b) (202) and the other ingredient optionally present (211) are fed to the extruder (205) through a third feed hopper (204) by means of a metering device (203).

Fig. 3 shows also a flow (206) exiting from the extruder (205) which is generally provided with a degassing unit schematically indicated by reference sign (207).

The elastomeric composition (213) is discharged from the extruder (205) by pumping it through an extruder die (208) by means of a gear pump (210) in the form of a continuous ribbon which may be transformed into a subdivided product operating as disclosed above (not represented in Fig. 3).

With reference to Fig. 4, "a" indicates an axial direction and "r" indicates a radial direction. For simplicity, Fig. 4 shows only a portion of the tyre, the remaining portion not represented being identical and symmetrically arranged with respect to the radial direction "r".

The tyre (100) comprises at least one carcass ply (101), the opposite lateral edges of which are associated with respective bead wires (102). The association between the carcass ply (101) and the bead wires (102) is achieved here by folding back the opposite lateral edges of the carcass ply (101)

around the bead wires (102) so as to form the so-called carcass back-folds (101a) as shown in Fig. 4.

Alternatively, the conventional bead wires (102) can be replaced with a pair of circumferentially inextensible annular inserts formed from elongate components arranged in concentric coils (not represented in Fig. 4) (see, for example, European patent applications EP 928,680 and EP 928,702). In this case, the carcass ply (101) is not back-folded around said annular inserts, the coupling being provided by a second carcass ply (not represented in Fig. 4) applied externally over the first.

The carcass ply (101) generally consists of a plurality of reinforcing cords arranged parallel to each other and at least partially coated with a layer of elastomeric compound. These reinforcing cords are usually made of textile fibres, for example rayon, nylon or polyethylene terephthalate, or of steel wires stranded together, coated with a metal alloy (for example copper/zinc, zinc/manganese, zinc/molybdenum/cobalt alloys and the like).

The carcass ply (101) is usually of radial type, i.e. it incorporates reinforcing cords arranged in a substantially perpendicular direction relative to a circumferential direction. Each bead wire (102) is enclosed in a bead (103), defined along an inner circumferential edge of the tyre (100), with which the tyre engages on a rim (not represented in Fig. 4) forming part of a vehicle wheel. The space defined by each carcass back-fold (101a) contains a bead filler (104) in which the bead wires (102) are embedded. An antiabrasive strip (105) is usually placed in an axially external position relative to the carcass back-fold (101a).

A belt structure (106) is applied along the circumference of the carcass ply (101). In the particular embodiment in Fig. 4, the belt structure (106) comprises two belt strips (106a, 106b) which  
5 incorporate a plurality of reinforcing cords, typically metal cords, which are parallel to each other in each strip and intersecting with respect to the adjacent strip, oriented so as to form a predetermined angle relative to a circumferential  
10 direction. On the radially outermost belt strip (106b) may optionally be applied at least one zero-degree reinforcing layer (106c), commonly known as a "0° belt", which generally incorporates a plurality of reinforcing cords, typically textile cords,  
15 arranged at an angle of a few degrees relative to a circumferential direction, and coated and welded together by means of an elastomeric material.

A side wall (108) is also applied externally onto the carcass ply (101), this side wall  
20 extending, in an axially external position, from the bead (103) to the end of the belt structure (106).

A tread band (109), whose lateral edges are connected to the side walls (108), is applied circumferentially in a position radially external to  
25 the belt structure (106). Externally, the tread band (109), which may be produced according to the present invention, has a rolling surface (109a) designed to come into contact with the ground. Circumferential grooves which are connected by  
30 transverse notches (not represented in Fig. 4) so as to define a plurality of blocks of various shapes and sizes distributed over the rolling surface (109a) are generally made in this surface (109a), which is represented for simplicity in Fig. 4 as  
35 being smooth.

A strip made of elastomeric material (110), commonly known as a "mini-side wall", may optionally be present in the connecting zone between the side walls (108) and the tread band (109), this mini-side wall generally being obtained by co-extrusion with the tread band and allowing an improvement in the mechanical interaction between the tread band (109) and the side walls (108). Alternatively, the end portion of the side wall (108) directly covers the lateral edge of the tread band (109). A underlayer which forms, with the tread band (109), a structure commonly known as a "cap and base" (not represented in Fig. 4) may optionally be placed between the belt structure (106) and the tread band (109). -

A layer of elastomeric material (111) which serves as an "attachment sheet", i.e. a sheet capable of providing the connection between the tread band (109) and the belt structure (106), may be placed between the tread band (109) and the belt structure (106).

In the case of tubeless tyres, a rubber layer (112) generally known as a "liner", which provides the necessary impermeability to the inflation air of the tyre, may also be provided in a radially internal position relative to the carcass ply (101).

The process for producing the tyre according to the present invention can be carried out according to techniques and using apparatus that are known in the art, as described, for example, in patents EP 199 064, US 4,872,822, US 4,768,937, said process including at least one step of manufacturing the green tyre and at least one step of vulcanizing this tyre.

More particularly, the process for producing the tyre comprises the steps of preparing, beforehand



and separately from each other, a series of semi-finished products corresponding to the various parts of the tyre (carcass plies, belt structure, bead wires, fillers, side walls and tread band) which are  
5 then combined together using a suitable manufacturing machine. Next, the subsequent vulcanization step welds the abovementioned semi-finished products together to give a monolithic block, i.e. the finished tyre.

10 Naturally, the step of preparing the abovementioned semi-finished products will be preceded by a step of preparing and moulding the various crosslinkable elastomeric compositions of which said semi-finished products are made: said  
15 crosslinkable elastomeric composition may be prepared according to the present invention or according to conventional techniques.

The green tyre thus obtained is then passed to the subsequent steps of moulding and vulcanization.  
20 To this end, a vulcanization mould is used which is designed to receive the tyre being processed inside a moulding cavity having walls which are counter-moulded to define the outer surface of the tyre when the vulcanization is complete.

25 Alternative processes for producing a tyre or parts of a tyre without using semi-finished products are disclosed, for example, in the abovementioned patent applications EP 928,680 and EP 928,702.

The green tyre can be moulded by introducing a  
30 pressurized fluid into the space defined by the inner surface of the tyre, so as to press the outer surface of the green tyre against the walls of the moulding cavity. In one of the moulding methods widely practised, a vulcanization chamber made of  
35 elastomeric material, filled with steam and/or

another fluid under pressure, is inflated inside the tyre closed inside the moulding cavity. In this way, the green tyre is pushed against the inner walls of the moulding cavity, thus obtaining the desired  
5 moulding. Alternatively, the moulding can be carried out without an inflatable vulcanization chamber, by providing inside the tyre a toroidal metal support shaped according to the configuration of the inner surface of the tyre to be obtained as described, for  
10 example, in patent EP 242,840. The difference in coefficient of thermal expansion between the toroidal metal support and the crude elastomeric material is exploited to achieve an adequate moulding pressure.

15 At this point, the step of vulcanizing the crude elastomeric material present in the tyre is carried out. To this end, the outer wall of the vulcanization mould is placed in contact with a heating fluid (generally steam) such that the outer  
20 wall reaches a maximum temperature generally of between 100°C and 230°C. Simultaneously, the inner surface of the tyre is heated to the vulcanization temperature using the same pressurized fluid used to press the tyre against the walls of the moulding  
25 cavity, heated to a maximum temperature of between 100°C and 250°C. The time required to obtain a satisfactory degree of vulcanization throughout the mass of the elastomeric material can vary in general between 3 min and 90 min and depends mainly on the  
30 dimensions of the tyre. When the vulcanization is complete, the tyre is removed from the vulcanization mould.

The present invention will be further illustrated below by means of a number of  
35 preparation examples, which are given for purely

indicative purposes and without any limitation of this invention.

EXAMPLES 1-5

Preparation of the masterbatches

5 Masterbatches were prepared by using a production plant as reported in Figure 1.

Masterbatches were prepared by using styrene-butadiene copolymer (SBR) and the thermoplastic polymers as shown in Table 1 (the amounts are  
10 expressed as % by weight of the total).

TABLE 1

| EXAMPLE        | 1  | 2  | 3  | 4  | 5  |
|----------------|----|----|----|----|----|
| SBR            | 75 | 75 | 75 | 75 | 75 |
| Topas® 6013    | 25 | -  | -  | -  | -  |
| Vestoran® 1100 | -  | 25 | -  | -  | -  |
| Edistir® 2560  | -  | -  | 25 | -  | -  |
| Vestodur® 2000 |    |    |    | 25 | -  |
| Questa® QA101  | -  | -  | -  | -  | 25 |

SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 40% by  
15 weight of styrene, mixed with 37.5% of oil (Europrene® 1721 - EniChem Elastomeri);

Topas® 6013: copolymer of norbornene and ethylene with norbornene content of 45% mol;  $T_g = 110^\circ\text{C}$ ; (commercialized by Ticona);

20 Vestoran® 1100: poly(2,6-dimethyl-1,4-phenylene ether);  $T_g = 116^\circ\text{C}$  (determined by ISO standard 306 - Vicat point); (commercialized by Degussa Hüls);

Edistir® 2560: atactic polystyrene;  $T_g = 97^\circ\text{C}$

(determined by ISO standard 306 - Vicat point);  
(commercialized by Polimeri Europa);  
Vestodur® 2000: polyethyleneterephthalate;  $T_m =$   
221°C - 226°C; (commercialized by Degussa Hüls);

- 5 Questa® QA101: syndiotactic polystyrene;  $T_m = 273^\circ\text{C}$ ;  
(commercialized by Dow Plastic).

The thermoplastic polymer, in the form of  
granules, was fed to the first feed hopper of a co-  
rotating twin-screw extruder Maris TM40HT having a  
10 nominal screw diameter of 40 mm and a L/D ratio of  
48.

The SBR rubber copolymer was obtained in the  
form of granules, having an average particle size of  
about 3 mm - 15 mm, by means of a rubber grinder.

- 15 In order to prevent reagglomeration, the  
obtained granules were dusted with silica.

Successively, the obtained granules were feed  
through a second and a third feed hopper (not  
represented in Fig. 1): specifically, 40% through a  
20 second feed hopper and 35% through a third feed  
hopper.

The feeding was carried out by means of a  
gravimetric feeder.

The working condition were the following:

25 EXAMPLES 1-2:

- twin screw speed: 300 rpm;
- temperature profile: 50-200-200-180-160-160-150-  
150-130-130-130-130°C;
- feeding rate 50 kg/h;
- 30 - elastomeric composition temperature measured at  
twin screw discharge: 180°C;

EXAMPLE 3:

- twin screw speed: 300 rpm;
- temperature profile: 50-180-180-180-160-160-150-  
35 150-130-130-130-130°C;

- feeding rate 50 kg/h;
- elastomeric composition temperature measured at twin screw discharge: 180°C;

EXAMPLE 4:

- 5 - twin screw speed: 400 rpm;
- temperature profile: 50-240-260-200-180-160-150-150-140-140-140-140°C;
- feeding rate 40 kg/h;
- elastomeric composition temperature measured at
- 10 twin screw discharge: 200°C;

EXAMPLE 5:

- twin screw speed: 500 rpm;
- temperature profile: 200-270-340-250-200-200-180-180-150-150-150-150°C;
- 15 - feeding rate 30 kg/h.

The masterbatch was discharged from the extruder in the form of a subdivided product (209a) by pumping it through an extruder die by means of a gear pump, said extruder die being provided with a perforated die plate equipped with knives (not represent in Fig. 1). The obtained product in subdivided form was then conveyed by air to a cooling device (not represented in Fig. 1).

20 The masterbatches thus obtained were analyzed with an optical microscope in order to evaluate the dispersion of the thermoplastic polymer within the diene elastomeric polymer, according to the following method.

Preparation of samples

30 A 3 g sample of each composition was pressure-molded in a Prestopress-Struers press (conditioning time = 15 min; pressure = 1 atm; maximum temperature = 110°C).

From the discs thus obtained, sections having a thickness of 5 µm were obtained using a Reichert-

Jung 2050 microtome equipped with a LN20 cryogenic unit (cutting temperature: -70°C). The sections thus obtained were placed on a slide previously cooled at -70°C.

5 Optical analysis

The sections thus prepared were observed with a transmission optical microscope with polarized light (Polyvar Met model; 10X lenses, multiplication factor = 1, equipped with polarizer and analyzer).

- 10 Twenty images for each sample were memorized through a JVC TK1280E videocamera with a Y/C connecting cable. The images were computer-analyzed (by means of an Image Pro Plus - Media Cybernetic software) measuring, for the field observed (mm<sup>2</sup>), the average  
15 number of aggregates present in the field observed and the average diameter values of said aggregates (μm). The results are reported in Table 2.

TABLE 2

| EXAMPLE                           | 1      | 2      | 3      | 4      | 5      |
|-----------------------------------|--------|--------|--------|--------|--------|
| Field observed (mm <sup>2</sup> ) | 13,000 | 13,000 | 13,000 | 13,000 | 13,000 |
| Average No. of aggregates         | 64     | 80     | 102    | 80     | 64     |
| Average diameter (μm)             | 10.5   | 12.5   | 10.5   | 13.6   | 16.2   |

20 EXAMPLES 6-12

Preparation of the elastomeric compositions

The elastomeric compositions given in Table 3

were prepared by using a production plant as reported in Fig. 1 (the amounts of the various components are given in phr).

5 All the ingredients, except for the sulphur and the accelerator, were mixed together in an internal mixer (of the laboratory type with tangential rotor (Banbury) model Pomini PL 1.6 for about 5 min (1st Step). As soon as the temperature reached  $145\pm 5^{\circ}\text{C}$ , the elastomeric composition was discharged. The  
10 sulphur and the accelerator were then added and mixing was carried out in an open roll mixer (2nd Step).

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TABLE 3

| EXAMPLE                          | 6 (*) | 7   | 8   | 9 (*) | 10  | 11  | 12  |
|----------------------------------|-------|-----|-----|-------|-----|-----|-----|
| 1 <sup>st</sup> STEP             |       |     |     |       |     |     |     |
| SBR                              | 100   | 70  | 70  | 100   | 70  | 100 | 70  |
| Carbon black                     | 60    | 60  | 60  | 60    | 60  | 60  | 60  |
| Zinc oxide                       | 2.5   | 2.5 | 2.5 | 2.5   | 2.5 | 2.5 | 2.5 |
| Stearic acid                     | 1     | 1   | 1   | 1     | 1   | 1   | 1   |
| Vestoran® 1100                   | 10    | -   | -   | -     | -   | -   | -   |
| MB Vestoran® 1100                | -     | 40  | -   | -     | -   | -   | -   |
| MB Topas® 6013 <sup>(1)</sup>    | -     | -   | 40  | -     | -   | -   | -   |
| Edistir® 2560                    | -     | -   | -   | 10    | -   | -   | -   |
| MB Edistir® 2560                 | -     | -   | -   | -     | 40  | -   | -   |
| MB Questra® QA101 <sup>(1)</sup> | -     | -   | -   | -     | -   | 40  | -   |
| MB Vestodur® 2000 <sup>(1)</sup> | -     | -   | -   | -     | -   | -   | 40  |
| Antioxidant                      | 2     | 2   | 2   | 2     | 2   | 2   | 2   |
| 2 <sup>nd</sup> STEP             |       |     |     |       |     |     |     |
| CBS                              | 2     | 2   | 2   | 2     | 2   | 2   | 2   |
| Sulphur                          | 1     | 1   | 1   | 1     | 1   | 1   | 1   |



(\*): comparative;

(1): addition of thermoplastic polymer without the use of masterbatch gave highly disomogeneous composition which cannot be tested.

5 SBR: styrene/butadiene copolymer, obtained by emulsion polymerization, containing 40% by weight of styrene, mixed with 37.5% of oil (Europrene® 1721 - EniChem Elastomeri);

Carbon black: N115 (Vulcan® 9 - Cabot);

10 Vestoran® 1100: poly(2,6-dimethyl-1,4-phenylene ether);  $T_g = 116^\circ\text{C}$  (determined by ISO standard 306 - Vicat point); (commercialized by Degussa Hüls);

MB Vestoran® 1100: masterbatch of Example-2;

15 MB Topas® 6013: masterbatch of Example 1;

Edistir® 2560: atactic polystyrene;  $T_g = 97^\circ\text{C}$  (determined by ISO standard 306 - Vicat point); (commercialized by Polimeri Europa);

MB Edistir® 2560: masterbatch of Example 3;

20 MB Questra® QA101: masterbatch of Example 5;

MB Vestodur® 2000: masterbatch of Example 4;

Antioxidant: phenyl-p-phenylenediamine;

CBS (accelerator): N-cyclohexyl-2-benzothiazyl-sulphenamide (Vulkacit® C2 - Bayer).

25 The static mechanical properties were measured on samples of the abovementioned elastomeric compositions vulcanized at  $170^\circ\text{C}$  for 30 min, according to ISO standard 37: the obtained results are given in Table 4.

30 Table 4 also shows the dynamic mechanical properties, measured using an Instron dynamic device in the traction-compression mode according to the following methods. A test piece of the cross-linked material having a cylindrical form (length = 25 mm;  
35 diameter = 14 mm), compression-preloaded up to a 10%

longitudinal deformation with respect to the initial length, and kept at the prefixed temperature (23°C, 100°C or 120°C) for the whole duration of the test, was submitted to a dynamic sinusoidal strain having  
5 an amplitude of  $\pm 3.33\%$  with respect to the length under pre-load, with a 10 Hz frequency. The dynamic mechanical properties are expressed in terms of dynamic elastic modulus ( $E'$ ) and  $\tan\delta$  (loss factor) values. As is known, the  $\tan\delta$  value is  
10 calculated as a ratio between the viscous modulus ( $E''$ ) and the elastic modulus ( $E'$ ), both of them being determined with the above dynamic measurements.

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TABLE 4

| EXAMPLE                       | 6 (*) | 7     | 8     | 9 (*) | 10    | 11    | 12    |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|
| STATIC MECHANICAL PROPERTIES  |       |       |       |       |       |       |       |
| Stress at break (MPa)         | n.d.  | 16.1  | 15.3  | 15.5  | 15.9  | 16.4  | 15.2  |
| DYNAMIC MECHANICAL PROPERTIES |       |       |       |       |       |       |       |
| Tandelta (23°C)               | 0.420 | 0.480 | 0.480 | 0.470 | 0.479 | 0.450 | 0.380 |
| Tandelta (100°C)              | 0.270 | 0.299 | 0.307 | 0.345 | 0.349 | 0.284 | 0.220 |
| Tandelta (120°C)              | 0.230 | 0.287 | 0.301 | 0.224 | 0.230 | 0.215 | 0.190 |
| E' (23°C)                     | 19.0  | 19.60 | 20.83 | 20.32 | 20.66 | 17.39 | 20.25 |
| E' (100°C)                    | 6.8   | 6.99  | 7.36  | 5.30  | 5.40  | 7.71  | 9.55  |
| E' (120°C)                    | 5.6   | 5.79  | 5.79  | 4.70  | 4.60  | 7.34  | 9.27  |

(\*) : comparative;

n.d.: not determined.

The results given in Table 4 show that the crosslinked manufactured products comprising the masterbatch of the thermoplastic polymer according to the present invention have:

- 5 - good stress at break (Examples 7, 8, 10, 11 and 12);
- good hysteresis properties at high temperatures (Examples 7 and 8): consequently, the elastomeric compositions of Examples 7 and 8
- 10 allow to obtain a high roadholding at high temperatures.

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CLAIMS

1. Method for producing a crosslinkable elastomeric composition comprising:
  - (a) at least one thermoplastic polymer selected from amorphous polymers having a glass transition temperature ( $T_g$ ) higher than 80°C or crystalline polymers having a melting temperature ( $T_m$ ) higher than 190°C;
  - (b) at least one diene elastomeric polymer;
- 5 said method comprising the following steps:
  - pre-mixing said thermoplastic polymer (a) with a portion of said diene elastomeric polymer (b) to obtain a masterbatch, said pre-mixing step being carried out at a
  - 10 temperature not lower than  $T_g$  or not lower than ( $T_m - 20^\circ\text{C}$ );
  - mixing the masterbatch obtained in said pre-mixing step (1) to the remaining portion of said diene elastomeric polymer (b).
- 20 2. Method for producing a crosslinkable elastomeric composition according to claim 1, wherein the portion of the diene elastomeric polymer (b) used is from 20% by weight to 90% by weight with respect to the weight of the diene elastomeric
- 25 polymer (b) present in the crosslinkable elastomeric composition.
3. Method for producing a crosslinkable elastomeric composition according to claim 2, wherein the portion of the diene elastomeric polymer (b)
- 30 used is from 30% by weight to 50% by weight with respect to the weight of the diene elastomeric polymer (b) present in the crosslinkable elastomeric composition.
4. Method for producing a crosslinkable elastomeric
- 35 composition according to any one of the

preceding claims, wherein the thermoplastic polymer (a) is present in the elastomeric composition in an amount of from 0.1 phr to 100 phr.

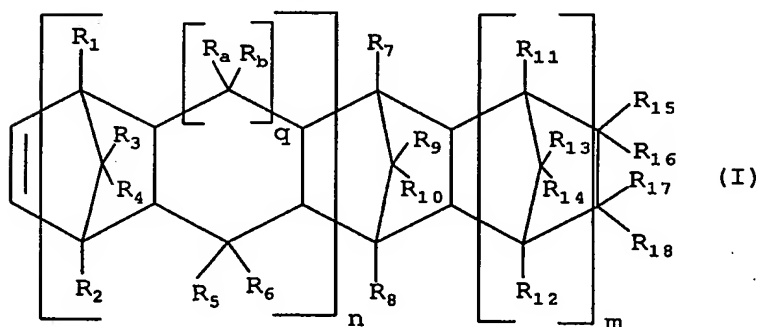
- 5      5. Method for producing a crosslinkable composition according to claim 4, wherein the thermoplastic polymer (a) is present in the elastomeric composition in an amount of from 3 phr to 60 phr.
- 10     6. Method for producing a crosslinkable composition according to claim 5, wherein the thermoplastic polymer (a) is present in the elastomeric composition in an amount of from 5 phr to 40 phr.
- 15     7. Method for producing a crosslinkable composition according to any one of the preceding claims, wherein the pre-mixing step comprises:
- feeding at least one thermoplastic polymer (a) into at least one extruder comprising a
  - 20       housing, at least one screw rotatably mounted in said housing including at least one feed opening and a discharge opening;
  - mixing said at least one thermoplastic polymer (a) at a temperature not lower than
  - 25        $T_g$  or not lower than  $(T_m - 20^\circ\text{C})$ ;
  - feeding at least one diene elastomeric polymer (b);
  - mixing said at least one diene elastomeric polymer (b);
  - 30       - dispersing said at least one thermoplastic polymer (a) into said at least one diene elastomeric polymer (b) to obtain a masterbatch;
  - extruding the obtained masterbatch through
  - 35       the discharge opening of said extruder.

8. Method for producing a crosslinkable composition according to claim 7, wherein the extruder is a co-rotating twin-screw extruder.
- 5 9. Method for producing a crosslinkable composition according to claim 7 or 8, wherein the masterbatch is obtained in the form of a continuous ribbon or in the form of a subdivided product.
- 10 10. Method for producing a crosslinkable composition according to any one of claims 7 to 9, wherein said at least one thermoplastic polymer (a) is dispersed in said masterbatch in the form of particles having an average diameter not higher than 20  $\mu\text{m}$ .
- 15 11. Method for producing a crosslinkable composition according to claim 10, wherein said at least one thermoplastic polymer (a) is dispersed in said masterbatch in the form of particles having an average diameter of between 8  $\mu\text{m}$  and 18  $\mu\text{m}$ .
- 20 12. Method for producing a crosslinkable composition according to any one of the preceding claims, wherein the thermoplastic polymer (a) is selected from: cycloolefin polymers, poly(phenylene ethers), styrene-based polymers, polyesters, polyamides, polyimides, polycarbonates, polysulfones, polyvinylchlorides, polymethyl(meth)acrylates, polyacrylonitriles, polyvinylpyrrolidones, aromatic polyketones, poly(alkylene oxides), aromatic polysulphides, perfluorurated polyalkylenes, or mixtures thereof.
- 30 13. Method for producing a crosslinkable composition according to claim 12, wherein the thermoplastic polymer (a) is selected from: cycloolefin polymers, poly(phenylene ethers), styrene-based
- 35

polymers, polyesters.

14. Method for producing a crosslinkable composition according to claim 13, wherein the cycloolefin polymer (b) is selected from:

- 5 (b-1) a cycloolefin random copolymer obtained by copolymerizing (i) at least one aliphatic  $\alpha$ -olefin and (ii) at least one cycloolefin represented by the following formula (I) and, optionally, (iii) a polyene;
- 10 (b-2) a ring-opening polymer of at least one cycloolefin represented by the following formula (I); and
- 15 (b-3) a hydrogenation product of a ring-opening polymer of at least one cycloolefin represented by the following formula (I):



wherein:

- 20 - n is 0 or a positive integer;
- m is 0 or a positive integer;
- q is 0 or 1;
- 25 - R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>a</sub> and R<sub>b</sub>, which may be equal or different from each other, represent a hydrogen atom, a halogen atom, or an aliphatic, an alicyclic or an aromatic



hydrocarbon group;

- R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, may be linked each other to form a monocyclic or polycyclic group which may have double bonds; and
  - 5        - R<sub>15</sub> and R<sub>16</sub>, or R<sub>17</sub> and R<sub>18</sub>, may together form an alkylidene group.
15. Method for producing a crosslinkable composition according to claim 14, wherein in the cycloolefin random copolymer (b-1) the aliphatic
- 10         $\alpha$ -olefin is an olefin of formula CH<sub>2</sub>=CH-R, in which R represents a hydrogen atom, a linear or branched alkyl group containing from 1 to 12 carbon atoms.
- 15        16. Method for producing a crosslinkable composition according to claim 13, wherein the poly(phenylene ethers) (PPE) are selected from thermoplastic engineering resins obtained by the oxidative coupling polymerization of alkyl substituted phenols.
- 20        17. Method for producing a crosslinkable composition according to claim 16, wherein the thermoplastic engineering resins include poly(2,6-dialkyl-1,4-phenylene ethers).
- 25        18. Method for producing a crosslinkable composition according to claim 13, wherein the styrene-based polymers have atactic, syndiotactic or isotactic configuration.
- 30        19. Method for producing a crosslinkable composition according to claim 18, wherein the styrene-based polymers are: polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(halogenated alkylstyrene), poly(alkoxystyrene), poly(vinyl benzoate), hydrogenated polymer thereof, or mixtures thereof.
- 35        20. Method for producing a crosslinkable composition

- according to claim 13, wherein the polyesters are selected from the polymer reaction products of at least one aliphathic or aromatic polycarboxylic acid ester of anhydride and at least a diol.
5. 21. Method for producing a crosslinkable composition according to claim 20, wherein the polyesters are: poly(trans-1,4-cyclohexylene-(C<sub>2</sub>-C<sub>6</sub>)-alkane dicarboxylates; poly(cis- or trans-1,4-cyclohexanedimethylene)alkanedicarboxylates;
- 10 poly-(C<sub>2</sub>-C<sub>4</sub>)-alkylene terephthalates; or mixtures thereof.
22. Method for producing a crosslinkable composition according to claim 12, wherein the thermoplastic
- 15 polymer (a), either amorphous or crystalline, contains functional groups selected from: hydroxy groups, carboxylic groups, anhydride groups, ester groups, silane groups, epoxide groups.
- 20 23. Method for producing a crosslinkable composition according to any one of the preceding claims, wherein the diene elastomeric polymer (b) has a glass transition temperature (T<sub>g</sub>) below 20°C.
- 25 24. Method for producing a crosslinkable composition according to claim 23, wherein the diene elastomeric polymer (b) is selected from: cis-1,4-polyisoprene, 3,4-polyisoprene, polybutadiene, optionally halogenated isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, styrene/1,3-butadiene copolymers, styrene/isoprene/1,3-butadiene copolymers, styrene/1,3-butadiene/acrylonitrile copolymers, or mixtures thereof.
- 30 25. Method for producing a crosslinkable composition

- according to any one of the preceding claims,  
wherein the elastomeric composition comprises at  
least one elastomeric polymer of one or more  
monoolefins with an olefinic comonomer or  
derivatives thereof (c).
- 5 26. Method for producing a crosslinkable composition  
according to claim 25, wherein the elastomeric  
polymer (c) is selected from: ethylene/propylene  
copolymers (EPR) or ethylene/propylene/diene  
10 copolymers (EPDM); polyisobutene; butyl rubbers;  
halobutyl rubbers; or mixtures thereof.
27. Method for producing a crosslinkable composition  
according to any one of the preceding claims,  
wherein at least one reinforcing -filler is  
15 present, in an amount of between 0.1 phr and 120  
phr, in the elastomeric composition.
28. Method for producing a crosslinkable composition  
according to claim 27, wherein the reinforcing  
filler is carbon black.
- 20 29. Method for producing a crosslinkable composition  
according to claim 27, wherein the reinforcing  
filler is silica.
30. Elastomeric composition comprising:
- from 1% to 65% of at least one thermoplastic  
25 polymer (a), said thermoplastic polymer (a)  
being selected from amorphous polymers  
having a glass transition temperature ( $T_g$ )  
higher than 80°C or crystalline polymers  
having a melting temperature ( $T_m$ ) higher than  
30 190°C;
  - from 35% to 99% of at least one diene  
elastomeric polymer (b);
- wherein said at least one thermoplastic polymer  
(a) is dispersed in said elastomeric composition  
35 in the form of particles having an average

diameter not higher than 20  $\mu\text{m}$ .

31. Elastomeric composition according to claim 30, comprising:

- 5. - from 10% to 40% of at least one thermoplastic polymer (a), said thermoplastic polymer (a) being selected from amorphous polymers having a glass transition temperature ( $T_g$ ) higher than 80°C or crystalline polymers having a melting  
10 temperature ( $T_m$ ) higher than 190°C;
- from 60% to 90% of at least one diene elastomeric polymer (b).

32. Elastomeric composition according to claim 30 or 31, wherein said at least one thermoplastic  
15 polymer (a) is dispersed in said elastomeric composition in the form of particles having an average diameter of between 8  $\mu\text{m}$  and 18  $\mu\text{m}$ .

33. Elastomeric composition according to any one of claims 30 to 32, wherein the thermoplastic  
20 polymer (a) is defined according to any one of claims 12 to 22.

34. Elastomeric composition according to any one of claims 30 to 33, wherein the diene elastomeric  
25 polymer (b) is defined according to claims 23 or 24.

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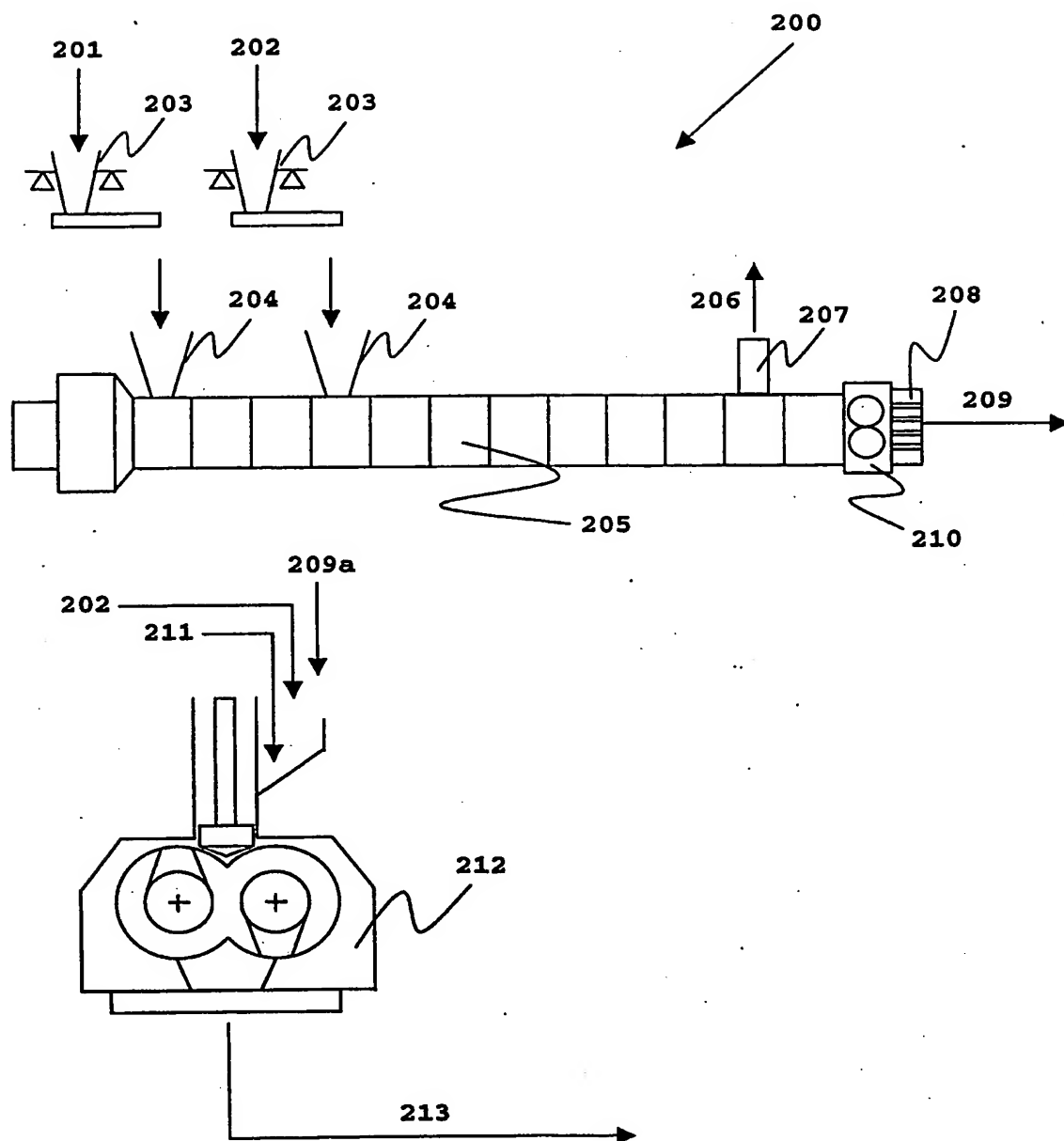


Fig. 1

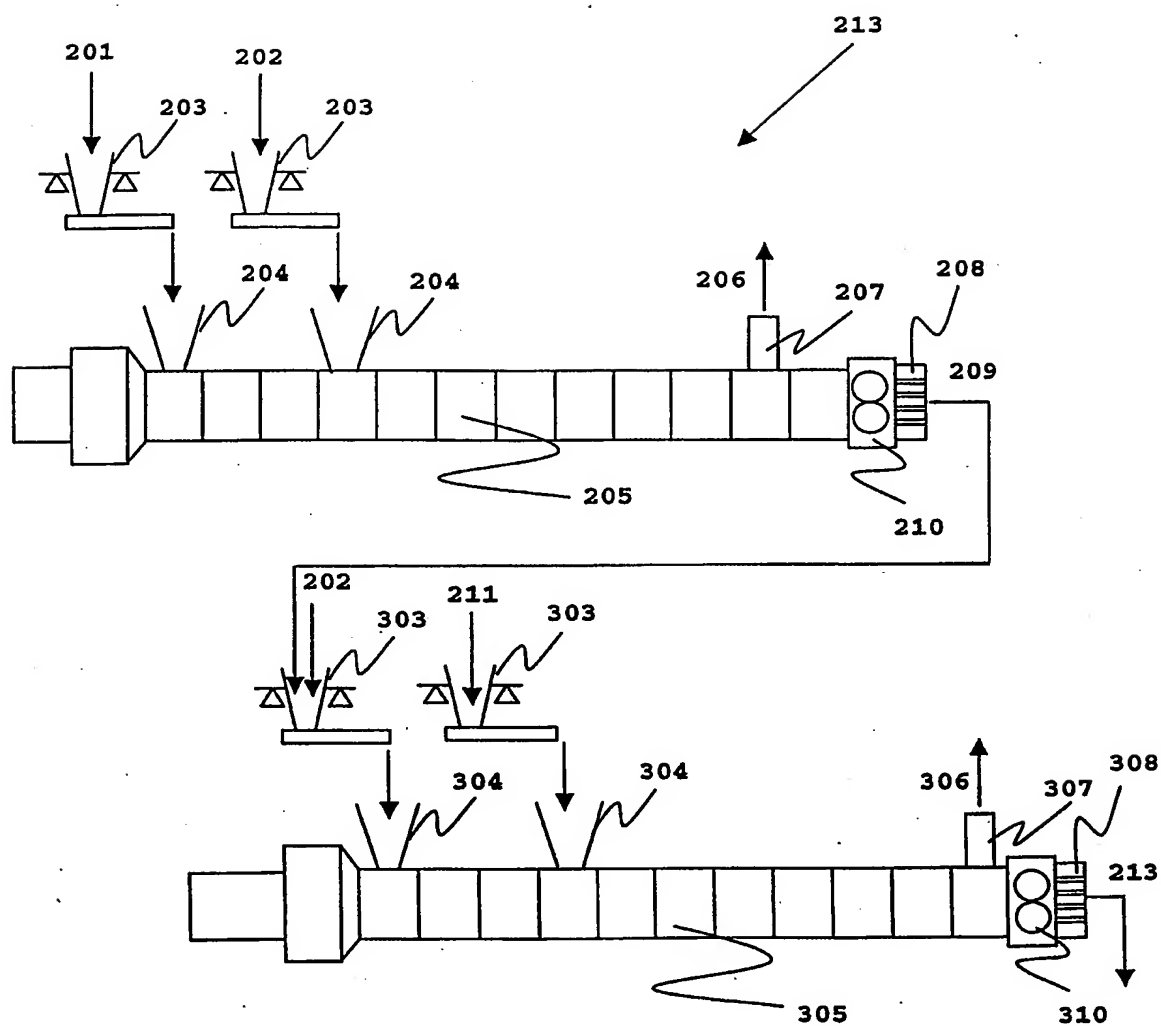
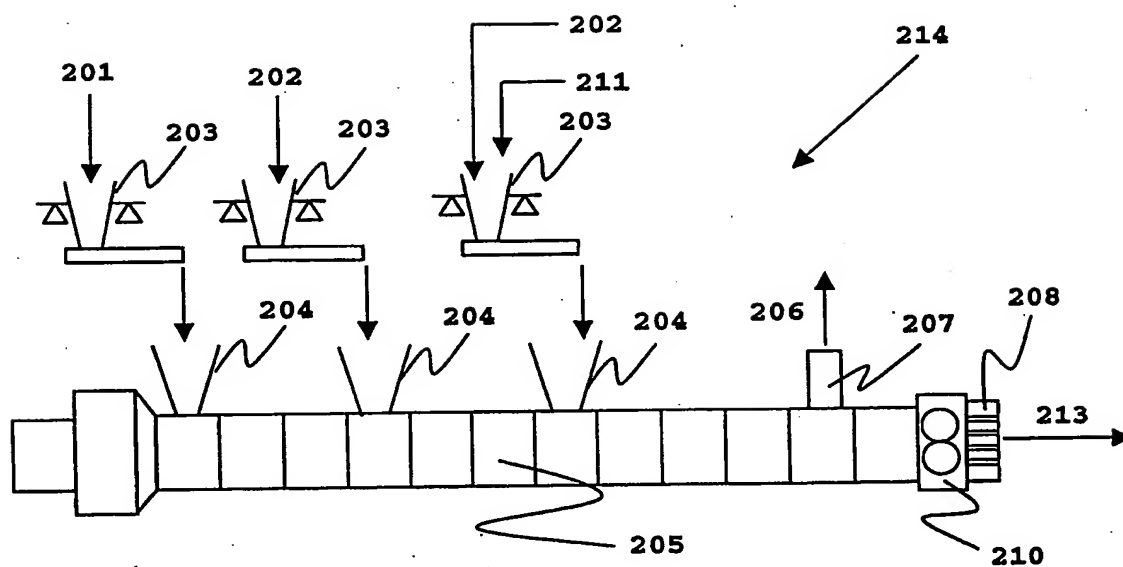


Fig. 2



**Fig. 3**

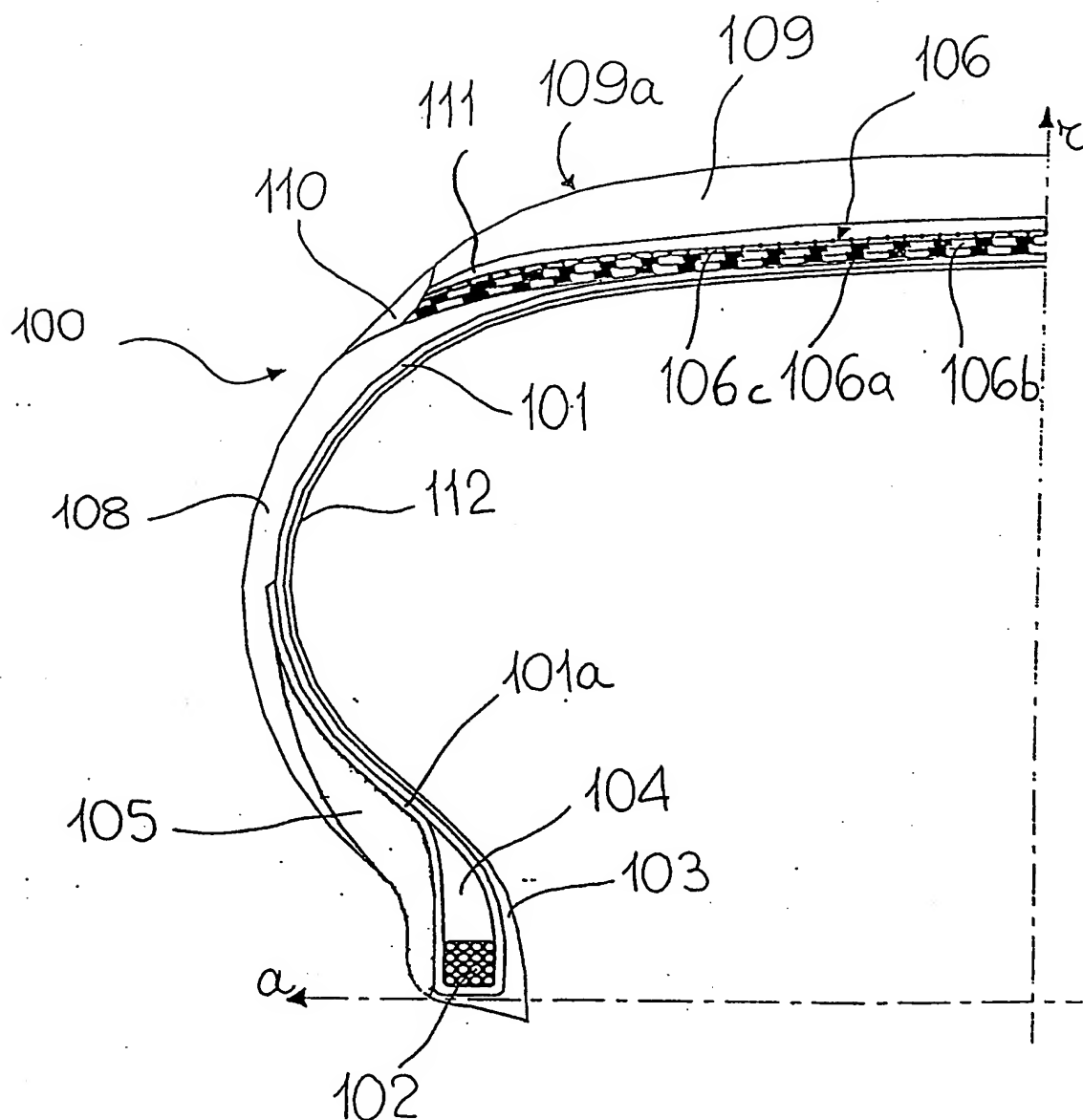


Fig. 4



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